Development of High Energy Cathode Materials

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Pacific Northwest National Laboratory

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Project ID#: ES056

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Overview

Timeline

- Start date: Oct. 2010
- End date: Sept.2011
- Percent complete:70%

Barriers addressed

- Low energy/low rate
- High cost
- Cycle life

Budget

- Total project funding
- FY10: 300K (100% DOE)

Partners

- SUNY Binghamton
- ANL
- University of Washington

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Objectives

- Investigate the thermal stability of lithium metal phosphate based cathode.
- Improve the performance of high voltage spinel $LiNi_{0.5}Mn_{1.5}O_4$.
- Develop high capacity cathode materials with stable cycling and high rate performances.

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Milestones (FY10-11)

- Synthesize $LiMnPO_4$ with high performance and investigate their thermal stability. – *Completed*
- Synthesize and optimize the performance of high voltage spinel ($LiNi_{0.5}Mn_{1.5}O_4$) – *On going*
- Synthesize nano structured vanadium based cathode with high capacity (>300 mAh/g) and rate capability. – *Completed*

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Approach

1. Investigation on the thermal stability of $LiMnPO_4$
   - Synthesize $LiMnPO_4$ in molten hydrocarbon
   - Use electrochemically cycled $LiMnPO_4$ electrode to replace chemically delithiated sample.
   - Investigate thermal stability of $LiMnPO_4$ using *in-situ* XRD, XPS, SEM-EDAX, TGA-DSC-MS characterizations

2. Synthesis of $LiNi_{0.5}Mn_{1.5}O_4$
   - Starting materials: all low cost (Li_2CO_3, $MnCO_3$, NiO).
   - Solid state synthesis: only milling and heating are involved. Easy scale-up.
   - Bulk modification: Cr doping
   - Surface modification: electrolyte additives, surface coating.
   - Investigation of morphology: particle size/morphology, packing density etc.

3. Synthesis of $Li_3V_2(PO_4)_3$ and LiV_3O_8
   - Two cost-effective solid-state-reaction methods for $Li_3V_2(PO_4)_3$
   - Facile solid-state-reaction method for LiV_3O_8

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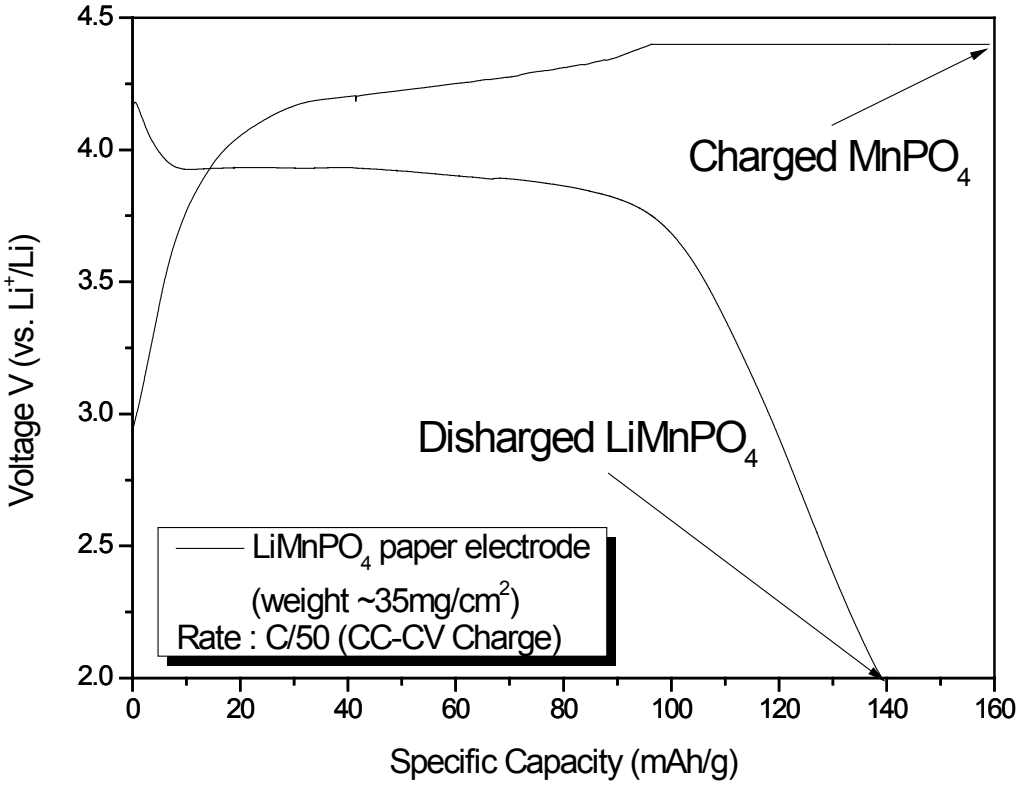
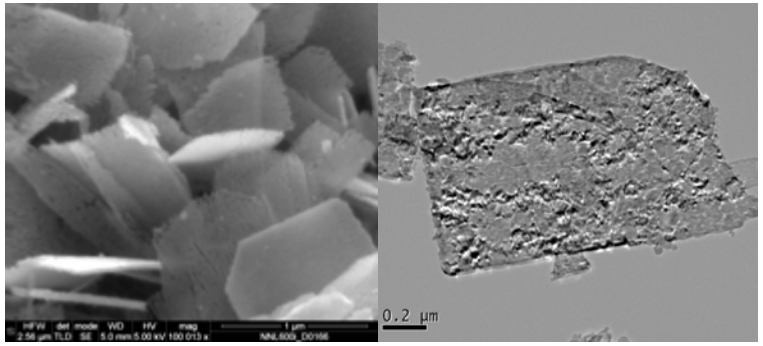
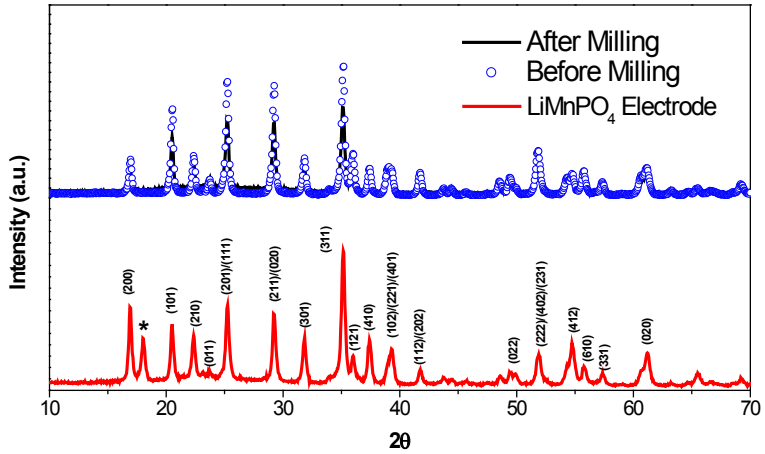
$LiMnPO_4$ Electrode for Thermal Stability







- Electrochemically active $LiMnPO_4$ nanoplates were obtained via molten hydrocarbon approach at 550ºC.
- $LiMnPO_4$ paper electrodes were made for thermal stability study of charged $MnPO_4$.
- Electrode comprised of $LiMnPO_4$: Ketjen black : PTFE = 70 : 22 : 8 wt%.
- Electrodes were collected after electrochemical charge and discharge for stability study.

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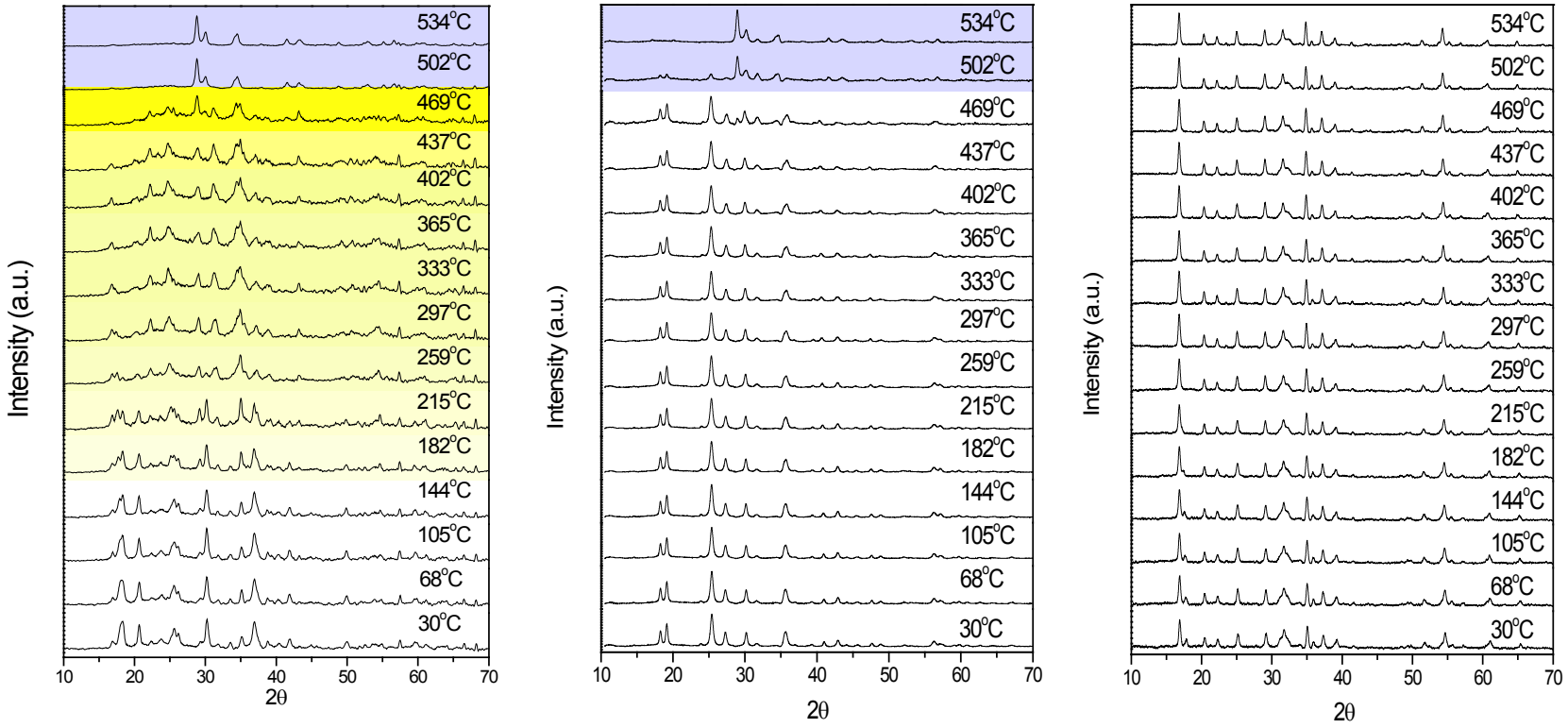
In-situ XRD on electrochemically cycled $LiMnPO_4$ and $MnPO_4 \cdot H_2O$ powder as a function of temperature



Charged $MnPO_4$ | $MnPO_4 \cdot H_2O$ powder | Discharged $LiMnPO_4$

- Charged $MnPO_4$ electrode undergo structural change (Jahn –Teller Distortion) above 180°C and reduction to $Mn_2P_2O_7$ above 470°C.
- $MnPO_4 \cdot H_2O$ powder undergo reduction to $Mn_2P_2O_7$ above 470°C.
- Discharge $LiMnPO_4$ electrode was stable up to 534°C.

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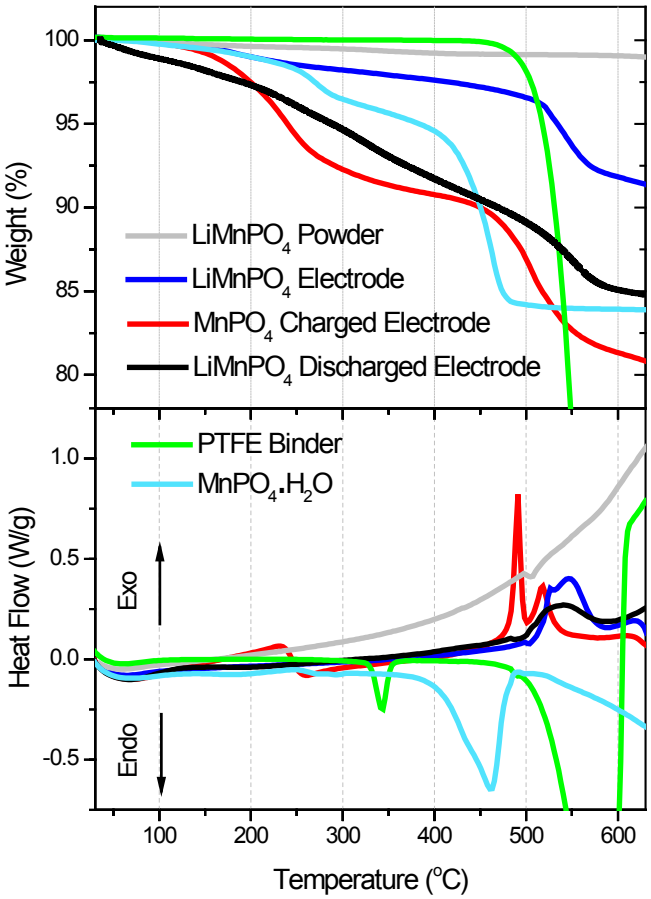
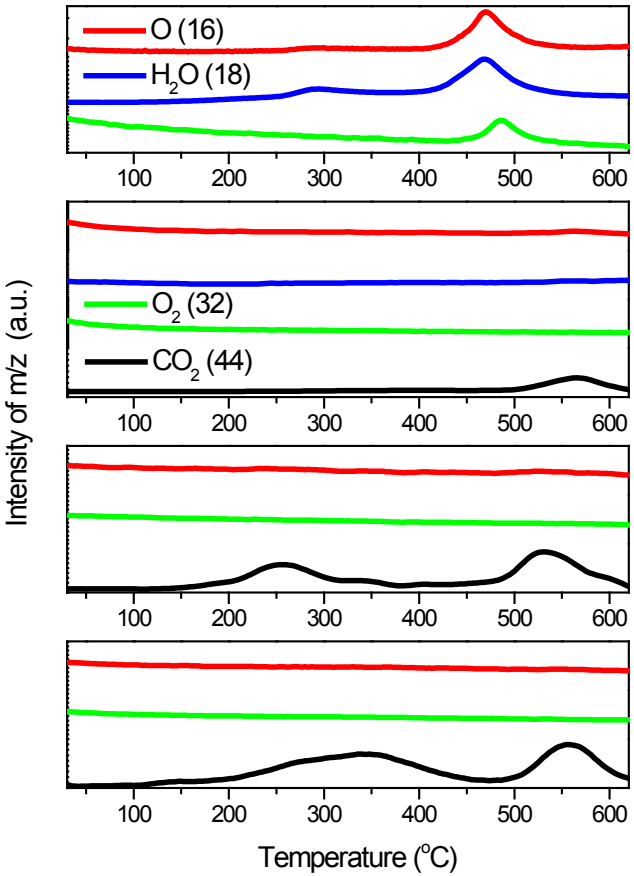
TGA-DSC-MS on $LiMnPO_4$ Electrode





$MnPO_4 \cdot H_2O$

As-prepared $LiMnPO_4$ electrode

Charged $MnPO_4$ electrode

Discharged $LiMnPO_4$ electrode

- DSC show sharp exothermic peak at 490°C related to oxygen release during reduction of $MnPO_4$ to $Mn_2P_2O_7$.
- No oxygen evolution is observed but most likely to be released as CO_2 ($C + O_2 \rightarrow CO_2$).

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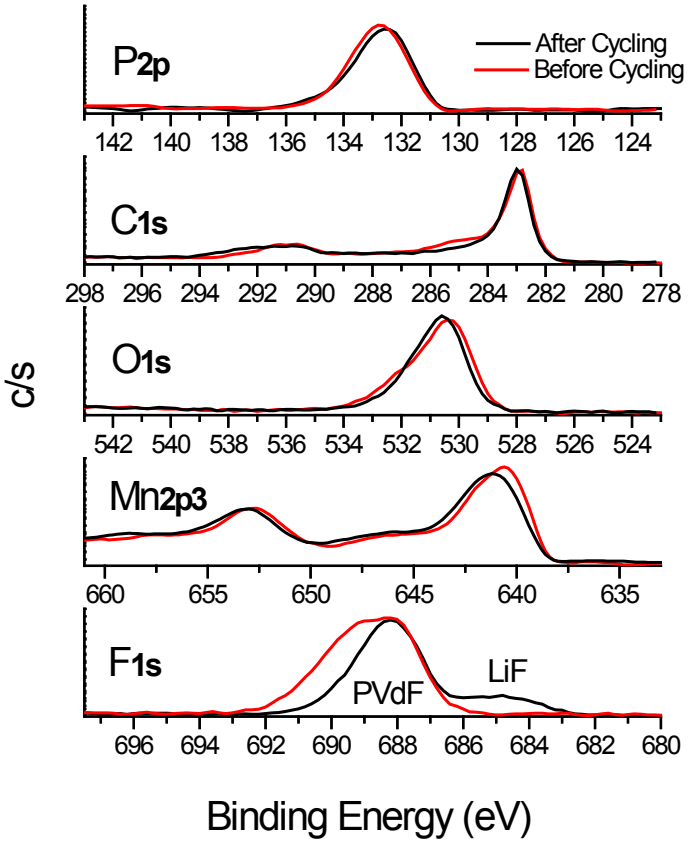
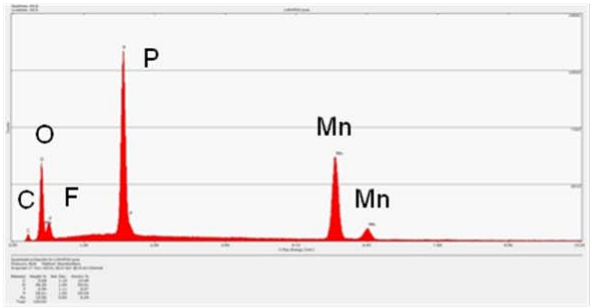
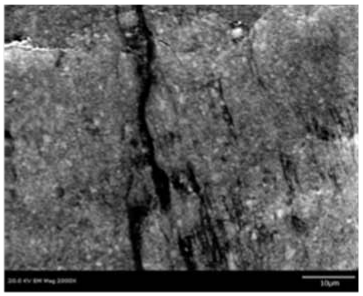
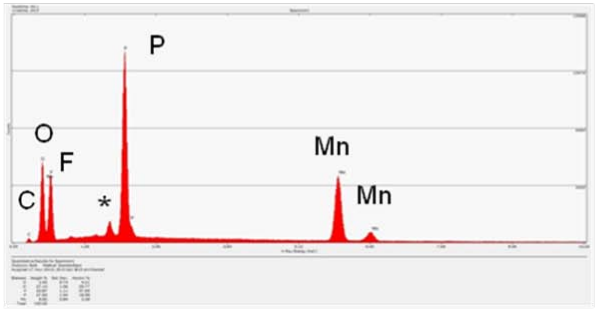
Surface Chemical Analyses on $LiMnPO_4$ Electrode

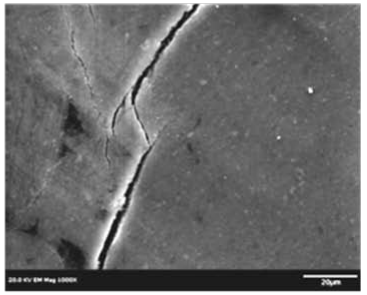






$LiMnPO_4$ electrode before electrochemical cycling





$LiMnPO_4$ electrode after 1st cycle (discharged state)

- $LiMnPO_4$ electrodes before and after electrochemical cycling show increase in F content from both XPS and EDAX.
- This indicate some type of SEI layer formation on the electrode which is responsible for the weight changes below 450°C.

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Thermal Stability Mechanism on Charged $MnPO_4$

$$MnPO_4 \underset{Pmna}{} \xrightarrow{150\sim180^{o}C} \underset{Jahn-Teller\ Distortion}{MnPO_4} \xrightarrow{490^{o}C} \frac{1}{2}\underset{C2/m}{Mn_2P_2O_7} + \frac{1}{2}O_2\uparrow$$

- From *in-situ* XRD, TGA-DSC-MS, XPS and EDAX results on the charged and discharged $LiMnPO_4$ cathode, the charged state of $MnPO_4$ undergoes structural changes due to Jahn-Teller effect at above 180°C and followed by reduction into $Mn_2P_2O_7$ at 490°C.
- The weight loss up to 450°C for charged $MnPO_4$ show similar behavior as that of discharged $LiMnPO_4$ cathode, indicating that the weight loss is due to decomposition of SEI layer formed during high-voltage electrochemical cycling process; this is similar to other cathodes reported.
- From the mass spectroscopy result during TGA analyses, no oxygen evolution was observed in charged/discharged $LiMnPO_4$ electrodes. The oxygen produced during reduction is released as CO_2 gas at 490°C after reacting with conductive carbon additive and is observed as sharp exothermic peak in the DSC scan.

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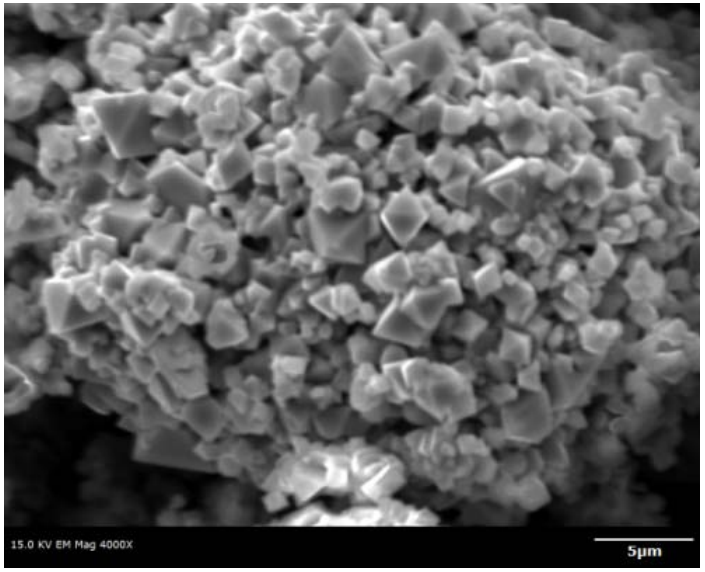
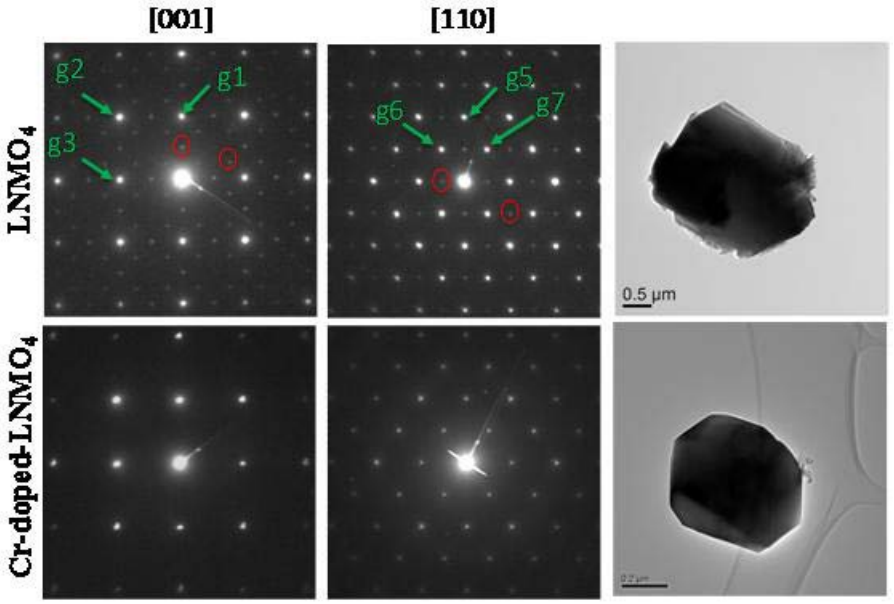
Cr Doping Increased Disorder





- ✓ As-prepared particles has a large particle size (>2 μm).
- ✓ Micron-sized samples further aggregate into secondary particles beneficial the practical application.
- ✓ $LiNi_{0.5}Mn_{1.5}O_4$: Mixed phases of disordered and ordered phase (the highlighted reflections are forbidden by $Fd\bar{3}m$).
- ✓ Cr-doped spinel: The super-lattice pattern is not observable.
- ✓ Cr substitution increases the disordering between Ni and Mn ions (consistent with the volume increase in Cr-doped spinel)

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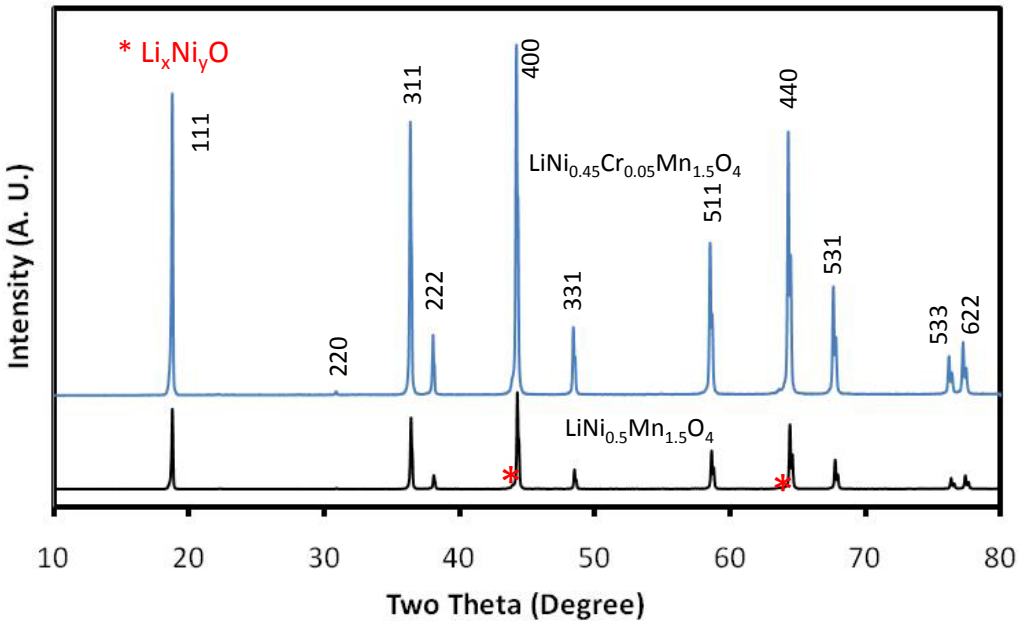
Cr Doping: Reduced Impurity Phase and Increased Disorder



- Both curves can be indexed into $Fd\bar{3}m$ (non-stoichiometry disordered $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$)
- Without doping: a small amount of Li_xNi_yO co-exist.
- After Cr doping: Impurity not detectable.
- Lattice parameter increases after Cr-doping (greater disorder)

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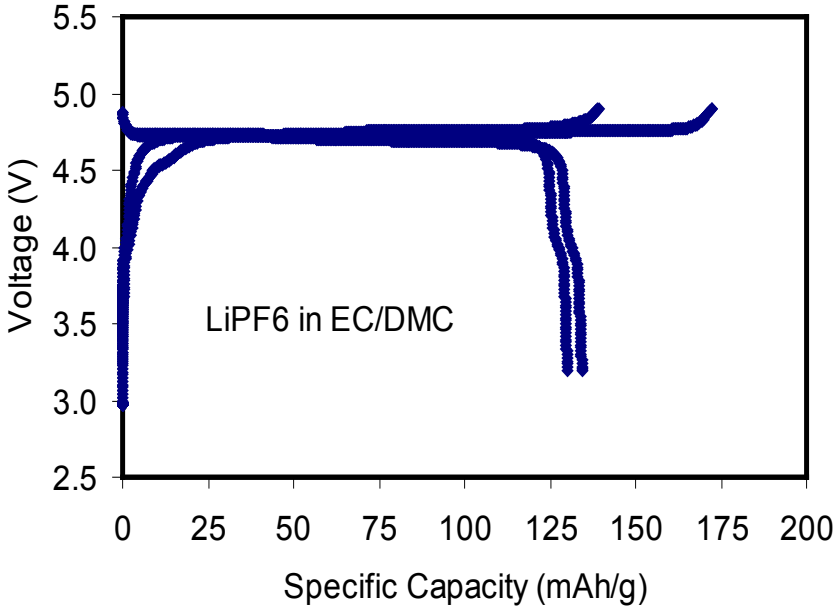
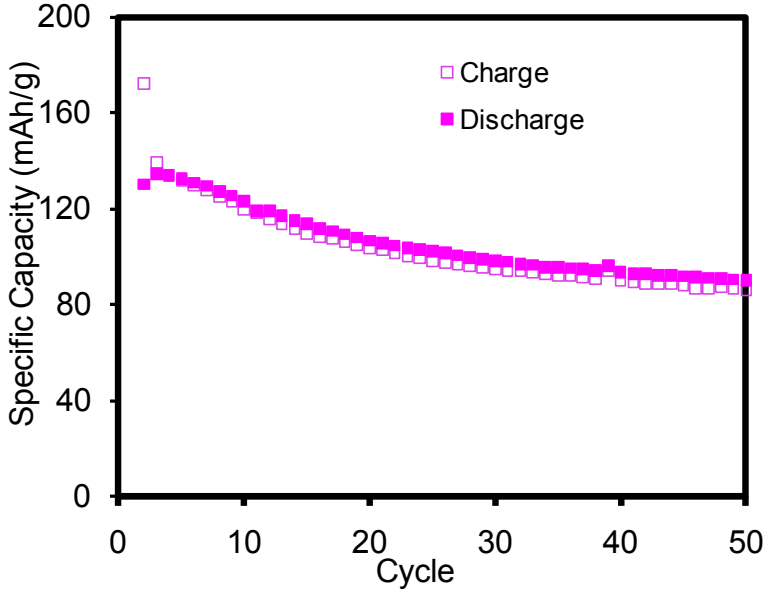
Electrochemical Performances of Undoped LNMO4





- Reversible capacity: 130 mAh/g; 1st cycle efficiency: 75%.
- Mn^{3+} content is minimal as reflected by the short 4.0 V plateau.
- Operation voltage is ~ 4.7 V with small polarization.
- Capacity fading is quick for pure $LNMO_4$.

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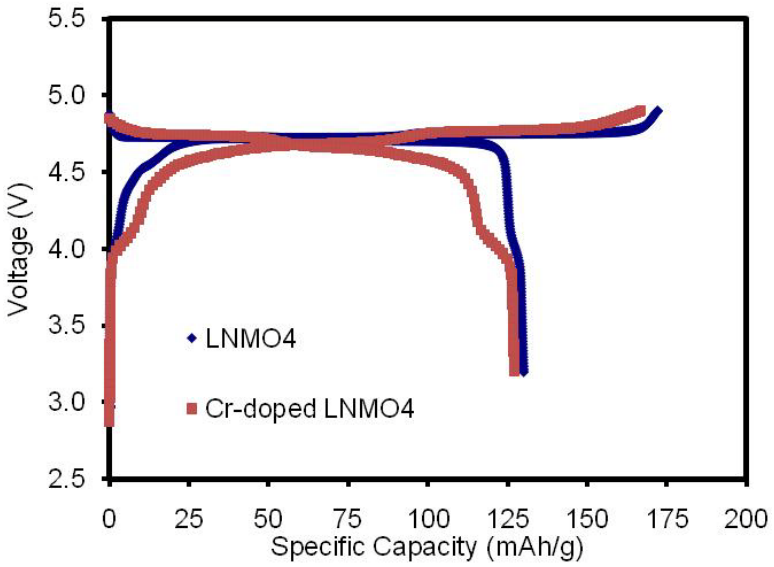
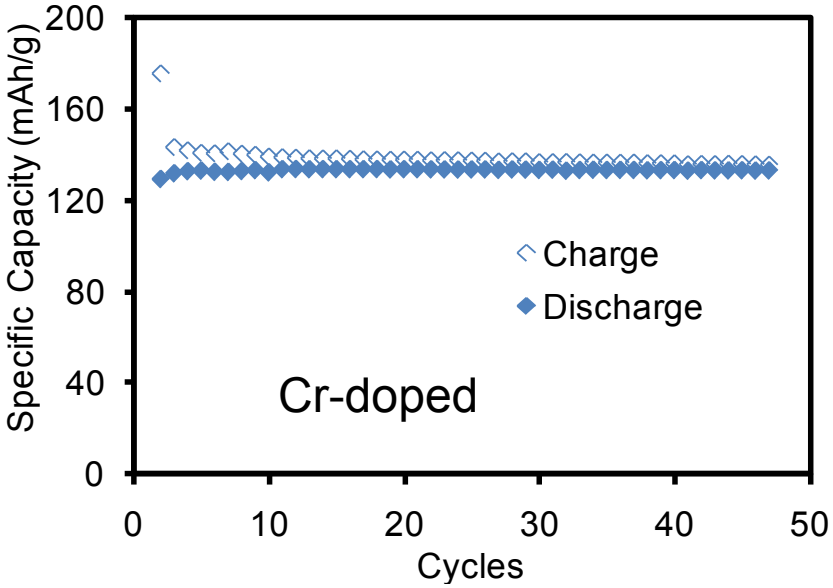
Electrochemical Performances of $LiNi_{0.45}Cr_{0.05}Mn_{1.5}O_4$





- After Cr-doping:
  - — Disordered phase is increased
  - — Mn^{3+} content is also increased.
  - — The initial capacity is slightly decreased due to Cr-doping
- Very stable cycling is maintained in Cr-doped spinel with reversible capacity at ca.130 mAh/g.

➢ The content of disordered phase (Mn^{3+}) is critical for the high performance spinel.

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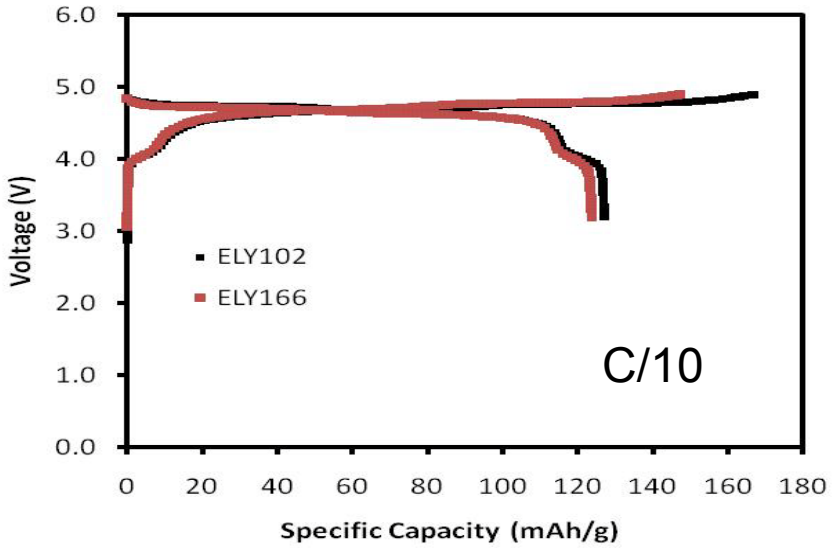
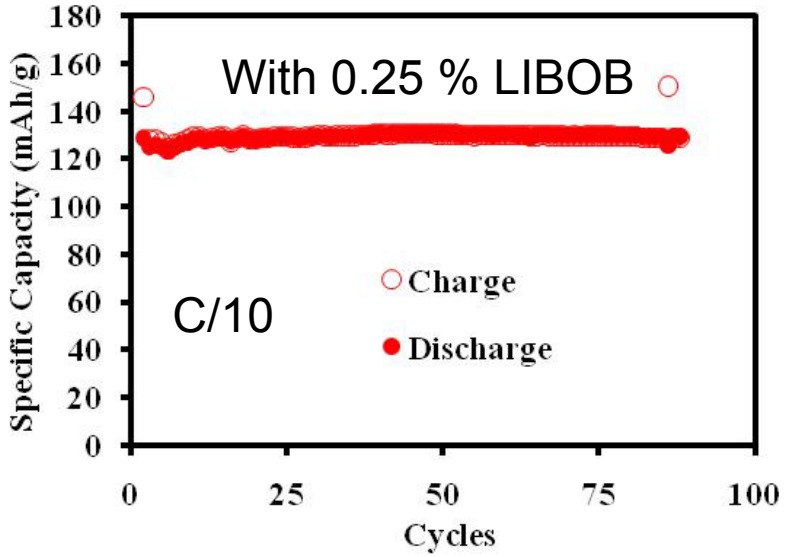
Electrolyte Additive Improved 1st Cycle Efficiency of $LiNi_{0.45}Cr_{0.05}Mn_{1.5}O_4$





- Without electrolyte additive, 1st cycle efficiency is low (~75%).
- LiBOB additive (0.25%) increased 1st cycle efficiency to 82%.
- Stable cycling almost without capacity fading in the first 80 cycles.

➢ Electrolyte additive is also important for high voltage spinel.

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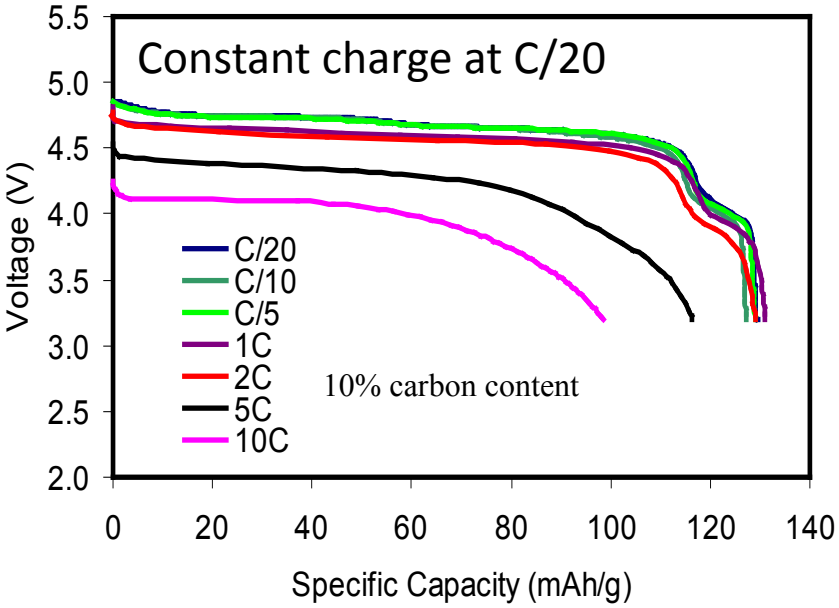
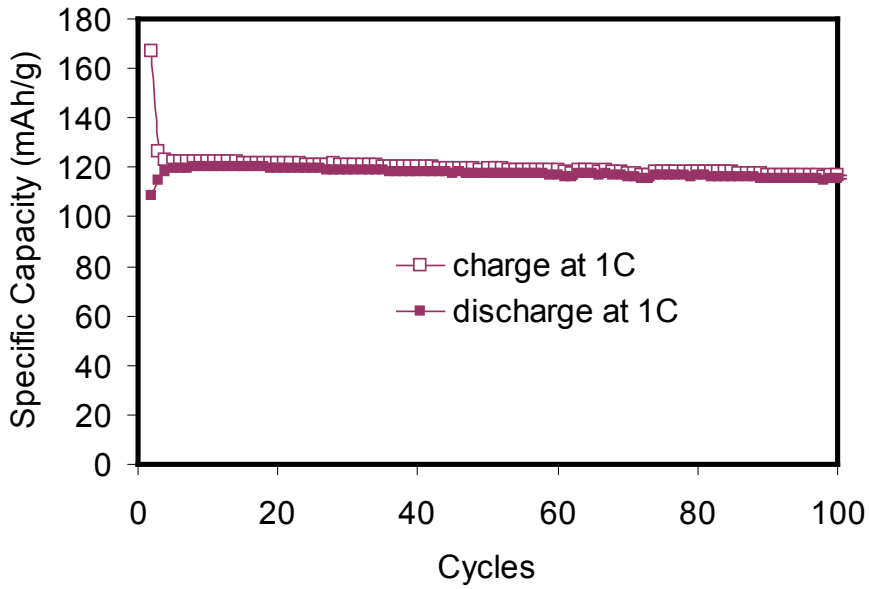
Rate Capability of $LiNi_{0.45}Cr_{0.05}Mn_{1.5}O_4$





- Good rate capability is observed at different rates.
- High voltage spinel does NOT have to go to nano size.
- No need to add a large amount of carbon for good high rate performance.

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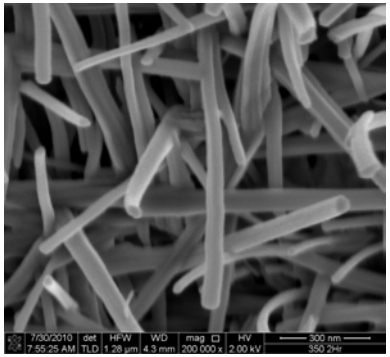
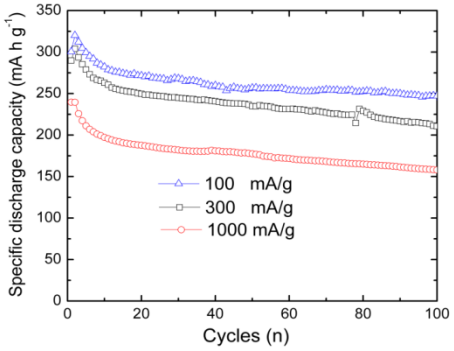
Nano-Engineering Improves Performance of Vanadium Based Cathode Materials

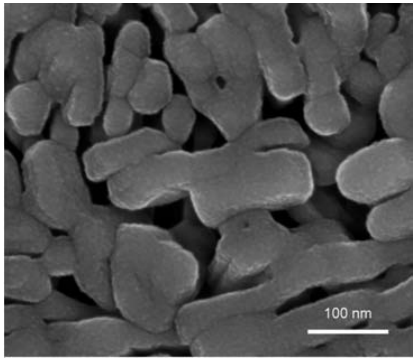
LiV_3O_8 nanorod

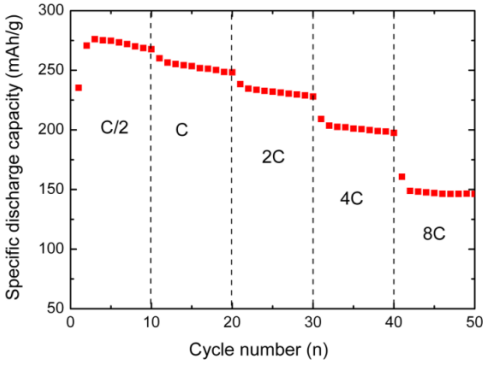




320 mAh/g at C/3

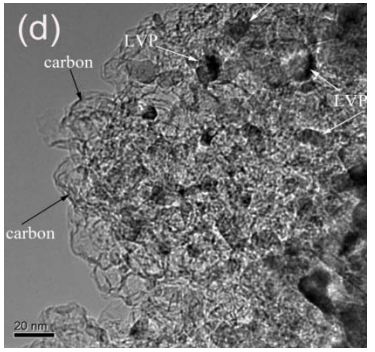
V_2O_5 nanorod

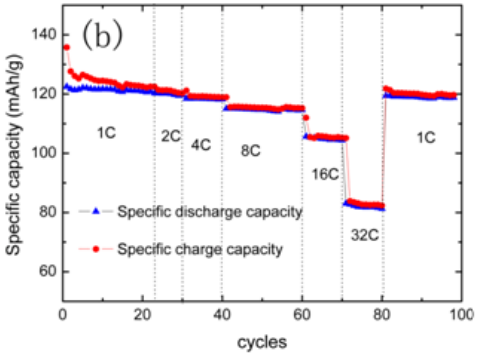




198 mAh/g at 4C

$Li_3V_2(PO_4)_3$ nano particle in carbon matrix





83 mAh/g at 32C rate

Synthesis controls material properties

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Collaboration and Coordination with Other Institutions

Partners:

- SUNY Binghamton (Academic): Magnetic properties of doped $LiMnPO_4$.
- ANL (Federal Lab): Provide alternative precursors for $LiNi_{0.5}Mn_{1.5}O_4$ synthesis.
- University of Washington (Academic): Characterization of vanadium based cathodes.

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Future Work - FY2011/FY2012

- Understand how the disordered content, residual Mn^{3+} and different dopants influence the electrochemical behavior of $LiNi_{0.5}Mn_{1.5}O_4$.
- Improve the first cycle efficiency and high temperature cycling performance of $LiNi_{0.5}Mn_{1.5}O_4$ through surface modification combined with appropriate electrolyte additives.
- Develop spinel/layered cathode composite with improved energy density.

Milestones (FY12)

- Optimization of synthesis approach for $LiNi_{0.5}Mn_{1.5}O_4$ and doped ones. –3/12
- Identification of electrolyte/additive for surface-modification on $LiNi_{0.5}Mn_{1.5}O_4$. – 6/12
- Synthesis of spinel/layered cathode composite. –9/12

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Summary

1. Improved the performance of high voltage spinel-$LiNi_{0.5}Mn_{1.5}O_4$.
   - A facile and cost-effective synthesis approach to prepare high voltage spinel.
   - Cycling performances is significantly improved after Cr-doping.
   - Appropriate electrolyte additives effectively improves the Coulombic efficiency of the first cycle.

2. Investigated the thermal stability of lithium metal phosphate based cathode.
   - Charged $MnPO_4$ is structurally stable up to 180^{o}C.
   - Oxygen release during reduction occurs at 490^{o}C.
   - Significant amount of SEI layer (~10 wt%) is formed during electrochemical charging of $LiMnPO_4$ cathode.

3. Developed vanadium-based high capacity cathode materials with stable cycling and high rate performances.
   - LiV_3O_8 with High rate performance: 239 mAh g^{-1} at 1000 mA g^{-1} rate and an average capacity fading rate of 0.34% per cycle for 100 cycles.

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